

Remarks

In view of the above amendments and the following remarks, reconsideration of the rejections and further examination are requested.

Claims 1, 4, 10 and 13 have been amended. Claim 2 has been cancelled without prejudice or disclaimer to the subject matter contained therein. Claim 19 has been added. Support for claim 19 can be found at least in Example 5 of the specification. Claims 1, 4-6, 10-13 and 19 are pending in the application.

The specification and abstract have been reviewed and revised to make a number of editorial revisions thereto. A substitute specification and abstract including the revisions have been prepared and are submitted herewith. No new matter has been added. Also submitted herewith are marked-up copies of the specification and abstract indicating the changes incorporated therein.

Claim 2 has been rejected under 35 U.S.C. §112, second paragraph, as being indefinite. Claim 2 has been cancelled without prejudice or disclaimer to the subject matter contained therein. As a result, withdrawal of the rejection under 35 U.S.C. §112, second paragraph, is respectfully requested.

Claims 1, 2, 4-6 and 10-13 have been rejected under 35 U.S.C. §103(a) as being unpatentable over Chahine (US 6,221,260) in view of Takahashi (“Effect of Shrinking Microbubble on Gas Hydrate Formation”).

This rejection is respectfully traversed and submitted to be inapplicable to the pending claims for the following reasons.

Claim 1 is patentable over the combination of Chahine in view of Takahashi, since claim 1 recites a method for collapsing microbubbles, the microbubbles having a diameter of 50 μm or less and floating in a solution and decreasing gradually in size by natural dissolution of a gas contained in the microbubbles, the method comprising accelerating a speed of microbubble size decrease and disappearance by applying a stimulation to the microbubbles, wherein a great amount of free radical species are released from a gas-liquid interface by increasing a charge density at the gas-liquid interface of the microbubbles. The combination of Chahine and Takahashi fails to disclose or suggest features currently recited in claim 1.

Initially, it is noted that claim 1 recites microbubbles decreasing gradually in size by natural dissolution of a gas contained in the microbubbles. In the rejection of claim 1, Chahine is relied upon as disclosing bubbles containing gas that correspond to this feature of claim 1. Specifically, section 22 of the Office Action indicates that column 15, lines 50-60 of Chahine discloses this feature.

Chahine at column 15, lines 50-60 discloses that oxidation efficiency can be increased by treating the liquid by entraining or saturating it with various gases (including ozone, argon, etc.) (i.e., dissolving the gas in the liquid) prior to cavitation of the liquid. The addition of the gas to the liquid in Chahine is to increase the number of cavitation bubbles.

Regarding this, generating cavitation bubbles in the same liquid for a long period of time decreases the amount of solution gas in the liquid. This is because the solution gas, such as air, in the liquid is emitted with cavitation and the emission of the solution gas causes the gradual decrease in the cavitation effect.

On the other hand, claim 1 is directed to the application of a stimulation to a microbubble that contains gas, not the cavitation of a liquid in which a gas is dissolved. Therefore, Chahine does not disclose or suggest this feature of claim 1. Further, the rejection of claim 1 relies on Takahashi as disclosing a microbubble having a diameter that is less than 50 μm and various characteristics of a microbubble. However, no combination of the disclosure of Takahashi with that of Chahine would render this feature of claim 1 obvious.

Further, claim 1 recites applying a stimulation to the microbubbles such that a great amount of free radical species are released from a gas-liquid interface by increasing a charge density at the gas-liquid interface of the microbubbles. In the rejection of claim 1, Chahine is relied upon as disclosing the increase of charge density at the gas-liquid interface of the microbubbles. Specifically, sections 8 and 23 of the Office Action indicate that Chahine at column 6, lines 1-10 discloses this feature.

Chahine at column 6, lines 1-10 discloses that one of the theories of cavitation is that the chemical reactions that occur when a bubble collapses are generated by electric discharge generated at the bubble collapse. Chahine also discloses other theories regarding why the chemical reactions occur, such as shock waves or hot spots. Additionally, Chahine at column 5, lines 37-54 discloses that cavitation also generates free radicals.

On the other hand, claim 1 recites that the increasing of a charge density at the gas-liquid interface of the microbubbles releases a great amount of free radical species. Clearly, the activity discussed in Chahine regarding the electric discharge at the collapse of a bubble differs from the charge density at a gas-liquid interface of a microbubble (i.e., while the microbubble is present in the solution). Therefore, Chahine does not disclose or suggest this feature of claim 1. Further, the rejection of claim 1 relies on Takahashi as disclosing a microbubble having a diameter that is less than 50 μm and various characteristics of a microbubble. However, no combination of the disclosure of Takahashi with that of Chahine would render this feature of claim 1 obvious.

Further, it is noted that it would not have been obvious to combine the disclosure of Takahashi directed to microbubbles with the disclosure of Chahine directed to cavitation bubbles.

Chahine relates to the generation of free radicals with the cavitation phenomenon and concerns enhancing the efficiency of the generation of free radicals. However, because Chahine utilizes cavitation, the bubbles have a relatively large diameter, and such bubbles are usually designated as "cavitation bubbles." Further, the characteristics of cavitation bubbles are different from those of microbubbles, such as those disclosed in Takahashi.

Cavitation bubbles are commonly generated by irradiating an ultrasonic wave in water and causing strong water flow. The ultrasonic wave and water flow cause a local pressure value to become lower than a saturated water vapor pressure to create the cavitation bubbles. Further, the cavitation bubbles include mostly water vapor. On the other hand, the microbubbles are generated by feeding gas into water. Thus, the microbubbles contain mostly the gas fed into water.

As noted above, the cavitation bubbles are generated by a decrease in the pressure. However, since the low pressure surrounding the cavitation bubbles is an instantaneous occurrence due to the ultrasonic wave and water moving, the cavitation bubbles instantly collapse because there is only water vapor pressure in the cavitation bubbles. On the other hand, the microbubbles are filled with gas and, as a result, have a much greater longevity.

Because of the significant differences between the cavitation bubbles that are the basis of the invention described in Chahine and the microbubbles of Takahashi, it is submitted that it

would not have been obvious to one of ordinary skill in the art to substitute the cavitation bubbles in Chahine with the microbubbles in Takahashi.

For all of the reasons discussed above, it is submitted that claim 1 is patentable over the combination of Chahine and Takahashi.

Further, claims 4-6, 10-13 and 19 are patentable over the combination of Chahine and Takahashi at least based on their dependency from claim 1.

Because of the above-mentioned distinctions, it is believed clear that claims 1, 4-6, 10-13 and 19 are allowable over the references relied upon in the rejection. Furthermore, it is submitted that the distinctions are such that a person having ordinary skill in the art at the time of invention would not have been motivated to make any combination of the references of record in such a manner as to result in, or otherwise render obvious, the present invention as recited in claims 1, 4-6, 10-13 and 19. Therefore, it is submitted that claims 1, 4-6, 10-13 and 19 are clearly allowable over the prior art of record.

In view of the above amendments and remarks, it is submitted that the present application is now in condition for allowance. The Examiner is invited to contact the undersigned by telephone if it is felt that there are issues remaining which must be resolved before allowance of the application.

Respectfully submitted,

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METHOD FOR COLLAPSING MICROBUBBLES

TECHNICAL FIELD

The present invention relates to a method of collapsing microbubble (microbubbles) that is useful in all technical fields, particularly in the technical field of water ~~processing~~ treatment.

BACKGROUND ART

Bubbles having a diameter of 50 μm or less (microbubbles) are known to have properties different ~~form~~ from those of normal bubbles, but the properties of the microbubbles ~~are~~ have not yet ~~to be~~ been well understood. For that reason, various microbubble generators under development recently only generate ~~microbubble~~ microbubbles of a gas in aqueous solution, and there is almost no invention that makes the most of the potential properties of microbubbles. An example of the traditional technology using microbubbles is the method described in JP-A-2002-143885 of accelerating the biological activity, metabolism, and consequently growth of organisms. However, although the invention has significant ~~advantageous~~ advantages in the field of cultivation of fish and shellfish, it does not disclose or suggest anything about collapsing microbubbles.

An example of the technology using the collapsing phenomenon of bubbles is a method of irradiating an ultrasonic wave ~~on bubbles~~ in aqueous solutions. However, the method is extremely ~~lower~~ low in efficiency because the bubbles for collapsing are generated by cavitational action of the ultrasonic wave itself, and has a problem of difficulty in ~~commercialization~~ practical usages because of its restricted

functions. ~~Most of the~~ Since cavitation bubbles are generated depending on the phenomenon of boiling at the low pressure region in the ultrasonic fields, the bubbles ~~then~~ contain ~~steam therein and~~ moisture (steam) as the main interior gas. And the bubbles ~~are present only~~ can exist for an extremely limited period of microseconds, because the bubbles containing condensable gas (moisture) collapse violently at the high-pressure region in the ultrasonic fields. ~~and~~ And thus, the method had ~~a problem~~ problems that it was not possible to use the ~~effects~~ effect of ~~the~~ another kind of gas ~~present in bubbles~~ as the main content and the effect of the electric charge formed at the gas-liquid interface ~~collapsing~~ of the bubbles.

SUMMARY OF THE INVENTION

An object of the present invention, which was made in view of the circumstances described above, is to provide a method for collapsing microbubbles, physical and chemical actions obtained by collapsing microbubbles, a method for collapsing the microbubbles by discharge, a method for collapsing the micro bubbles by ultrasonic wave, a method for collapsing the microbubbles by swirling current, a method for collapsing the microbubbles by using positive or negative pressure, and a method for collapsing the microbubbles by using the catalytic reaction of an oxidizer, as well as a method of decomposing microbes, viruses and the like, which ~~were~~ was considered to be impossible by traditional technology.

The object of the present invention is accomplished by a method for collapsing microbubbles, characterized in that, in the step of the microbubbles having a diameter of 50 μm or less floated in a solution decreasing gradually by natural

dissolution of the gas contained in the microbubbles and disappearing finally, the microbubbles are disappeared by accelerating the speed of the microbubble size decrease by applying a stimulation to the microbubbles.

The object of the present invention is also accomplished more effectively by forming an ultrahigh-pressure ultrahigh-temperature region inside in an adiabatic compression-like change of the microbubbles caused by decrease of the ~~microbubbles size; the~~ size. The electric charge density at the interface of the microbubbles increases rapidly and a great amount of free radical species are released from the gas-liquid ~~interface; free~~ interface. Free radical species such as active oxygen species for decomposition of the substances present inside the microbubbles or in the area surrounding the microbubbles are generated by collapsing the ~~microbubbles; the~~ microbubbles. The method gives rise to a compositional change of the chemical substances dissolved or floated in the solution; or the method sterilizes microorganisms such as microbes, viruses, and others present in the solution.

Further, the object of the present invention is also accomplished more effectively by applying the stimulation ~~is as~~ as electric discharge in a container containing a microbubble-containing solution generated by using a discharger; the stimulation ~~is as an~~ as ultrasonic wave irradiated into a container containing a microbubble-containing solution by an ultrasonicator; or the ultrasonicator is connected to the container between a microbubble-containing solution outlet port of a microbubble generator connected to container and an intake of the microbubble generator and the stimulation is given by continuous irradiation of ultrasonic wave into the container by the ultrasonicator.

When a circulation pipe is connected to a container containing a microbubble-containing solution, the object of the present invention is also accomplished more effectively by applying the stimulation—~~is~~ as compression, expansion and swirling current generated by circulating part of the microbubble-containing solution in the container by the circulation pump and making the solution—~~path~~ pass through an orifice or porous plate having a single or multiple holes installed in the circulation pipe; the circulation pump gives a positive pressure of 0.1 MPa or more to the discharge side; the circulation pump gives a negative pressure lower than the environmental pressure to the intake side; or when a circulation pipe is connected to the container containing a microbubble-containing solution, the stimulation is compression, expansion and swirling current generated by feeding the microbubble-containing solution in the container into the circulation pipe and making the solution—~~path~~ pass through an orifice or porous plate having a single or multiple holes installed in the circulation pipe.

The object of the present invention is achieved more effectively by applying the—~~the~~ stimulation—~~is~~ as forcibly internal circulation, in the pipe for feeding the microbubble-containing solution generated by a microbubble generator to a container, of making the microbubble-containing solution discharged from the microbubble generator pass through a punching plate installed in the pipe,—~~taken~~ taking in part of the microbubble-containing solution from an intake installed between the punching plate and the container and feeding it into a pump, feeding the microbubble-containing solution into the pump, discharging it—~~form~~ from an outlet port installed between the microbubble generator and the punching plate, and making it

pass through the punching plate once again; or the pump gives a positive pressure of 0.1 MPa or more to the discharge side; the pump gives a negative pressure lower than the environmental pressure in the upstream pipe; the stimulation is a catalytic reaction generated by allowing an oxidant to react in the presence of a ~~catalyst~~, catalyst, the catalyst ~~is~~ being copper and the oxidizer ~~is~~ being ozone or hydrogen peroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing the results of measuring the zeta potential of microbubbles in distilled water.

Figure 2 is a diagram showing the electrification mechanism of microbubbles in water.

Figure 3 is a graph showing the relationship between the time period until microbubbles decrease ~~of the microbubble~~ in size and disappear and the bubble diameter of the microbubbles.

Figure 4 is a graph showing the increase in zeta potential associated with decrease of microbubbles size.

Figure 5 is a side view of an apparatus for collapsing the microbubbles by using a discharger.

Figure 6 is a side view of an apparatus for collapsing the microbubbles by using an ultrasonicator.

Figure 7 is a side view of an apparatus for collapsing the microbubbles by using swirling current.

Figure 8 is a side view of an apparatus for collapsing the microbubbles by using positive or negative pressure.

Figure 9 is a partial side view of the apparatus for collapsing the microbubbles by using positive or negative pressure.

Figure 10 is a side view of an apparatus for collapsing the microbubbles in the reaction of an oxidizer in the presence

of a catalyst.

Figure 11 is an ESR spectrum of the free radicals generated during collapsing the microbubbles.

EXPLANATION OF ~~NUMERALS~~ REFERENCE NUMBERS

- 1 Container
- 2 Discharger
- 21 Anode
- 22 Cathode
- 3 Microbubble generator
- 31 Intake
- 32 Microbubble-containing solution outlet
- 4 Ultrasonicator
- 5 Circulation pump
- 6 Orifice (porous plate)
- 7 Oxidizer-supplying unit
- 8 Catalyst
- 9 Pump
- 10 Punching plate
- 11 Intake
- 12 Outlet

~~BEST MODE OF CARRYING OUT~~ DETAILED DESCRIPTION OF THE
INVENTION

As shown in Figure 1, as ~~a~~ one of the most important
physical-property properties of microbubbles for this invention,
microbubbles in distilled water ~~have~~ are negatively charged with
an electric potential of ~~approximately~~ between -30 to -50 ~~mV~~
independently of mV. There is no relationship recognized
between the magnitude of the potential and the bubble diameter
of bubbles. Thus, ~~for example in water,~~ as shown in Figure 2, ~~a~~

the microbubble has a structure in which the bubble surface is surrounded by negative ions such as of OH^- , which in turn are surrounded additionally by cations such as of H^+ (H_3O^+).

In addition, a microbubble has a greater specific surface and a higher internal pressure than a normal bubble, because the surface tension acts more effectively. It is generally accepted academically that the internal pressure of a microbubble reaches as high as thousands of atmospheric pressures when it disappears.

~~Microbubbles are known to be~~A microbubble is a tiny bubble and its rising speed is normally lower~~rate of climb~~ than normal ~~bubbles~~ bubbles, and it is superior in gas dissolving~~capacity~~ ability (natural dissolution). ~~Thus, normal bubbles, when generated in water, rising~~Normal bubbles rise toward the liquid surface~~direction~~ directly and burst at the liquid surface, while microbubbles~~rising~~ rise more slowly than normal bubbles and have a superior~~dissolving capacity, thus resulting in gradual~~ gas dissolution ability. Thus, microbubbles gradually decrease in~~the bubble~~ diameter and finally~~disappearance of the bubbles~~ disappear. Figure 3 shows the~~results of measuring the time until the~~ change of microbubble diameter as a function of time. The microbubble decreases~~of its~~ in size and finally disappears. The microbubble having a smaller bubble diameter ~~shows~~ exhibits rapid natural dissolution and has a shorter time of decrease of microbubble size and to disappearance of the microbubble by natural dissolution. The most effective~~maximum~~ driving force~~for dissolving the~~ of gas in dissolution of microbubbles is the self-compression~~effect by~~ due to the surface tension. The increase in pressure of the interior gas from the ambient~~buildup inside the microbubble with respect to environmental~~ pressure can be estimated by the Young-Laplace's

Formula Equation.

(Formula 1)

$$\Delta P = 4\sigma/D$$

In the Formula equation, ΔP represents the degree of pressure difference between surrounding water and the interior gas buildup; σ , surface tension, tension; and D , bubble diameter. In distilled water at room temperature, the pressure buildup difference is approximately 0.3 atmospheric pressure in a microbubble microbubbles having a diameter of 10 μm and approximately 3 atmospheric pressures in the bubble bubbles having a diameter of 1 μm . The compressed gas in a self-compressed bubble, which behaves in water according to the Henry's law in gas phase, microbubbles dissolves efficiently in ambient water accordingly to Henry's law.

On the other hand, the decreasing speed of the microbubble size decrease by natural dissolution rises can be accelerated by application the applications of a physical stimulation stimulations such as discharge, ultrasonic wave, or swirling current to the microbubble, and thus, microbubble. As a result of this application, the microbubble is decreases in size with adiabatic compression and disappears (collapsing). Adiabatic compression of the microbubble then gives rise to an extreme reaction field at ultrahigh temperature and ultrahigh pressure when the microbubble disappears (collapsing).

As described above, an bubble present the microbubbles in distilled water is charged negatively but there are are negatively charged. But the observation of the zeta potential of microbubbles indicates that the saturated electric charges formed at the gas-liquid interface is according to the environmental conditions such as pH, pH of water, which can be observed by the zeta potential of the microbubble. The This type

~~of electric charges~~ electrical charge is not due to electrolytic ions ~~and others~~ in water, but ~~are~~ is based on the structural factor of water itself. That is, the ~~electric charges are~~ charge is generated by interfacial adsorption of OH^- and H^+ ~~ions, based on ions~~ due to the difference between of the hydrogen-bonded network structure at between the gas-liquid interface and the ~~structure of bulk of the water~~. The ~~structure~~ structures formed ~~also has an action to~~ by the adsorption of the ions suppress thermal molecular movement at the interface, and ~~thus~~, it takes time of about several seconds to go back to the equilibrium condition ~~after when~~ the electric charge density fluctuates has fluctuated.

~~Decrease of the~~ The natural dissolution of the interior gas leads to the decrease in bubble size by natural dissolution of the microbubble is accompanied with and decrease in the surface area of ~~gas-liquid~~ gas-water interface. ~~The~~ And, the surface area of the gas-liquid interface decreases more rapidly as the bubble becomes smaller, as shown in Figure 3. When the decreasing speed of the decrease in the surface area of gas-liquid interface is lower is not so high, the electric charge density at the gas-liquid interface ~~remains in~~ does not change notably from the condition almost in equilibrium condition. However, as shown in Figure 4, when the bubble diameter ~~decreases~~ has decreased to 10 μm or ~~less, dissipation of electric charge cannot catch up the speed of the size decrease, which is observed as an increase in~~ less and the decreasing speed of the surface area has become much higher (see Figure 3), it is difficult for the gas-water interface to maintain the zeta potential associated with deviation from in its equilibrium condition. However, ~~the decrease in~~ in the case of the microbubbles under natural condition, the decreasing speed of the surface area of gas-

~~liquid interface by natural dissolution~~ is not so ~~rapid~~ high, and the value of electric charge density remains up to several times larger than that in equilibrium, even at the point immediately before disappearance.

In contrast, ~~during the collapsing microbubbles according to the present invention~~ discloses the method to accelerate the decreasing speed, ~~the speed of, the decrease in the surface area of the gas-liquid interface is very high area,~~ and the electric charge remains at the shrinking interface and the zeta potential as it is without dissipation and deviates from equilibrium, resulting in generation of a region extremely higher in its equilibrium. As a result, ~~the electric~~ electrical charge density of the interface becomes extremely high. When the ~~bubble microbubble~~ having a diameter of 20 μm decreases ~~into the microbubble~~ to the size of 0.5 μm or less by collapsing, the electric charge density rises to a value as high as 1,000 times larger than that in equilibrium.

The extremely high-density electric charge formed by collapsing is in a non-equilibrium condition and extremely ~~instable~~ unstable, and the system returns ~~back to a~~ to its stable state ~~in~~ though a ~~phenomenon~~ different method from a simple dissipation of the charge. Thus, an extremely large potential gradient is formed between the bubble interface and its surrounding area ~~in~~ during the collapsing process, and the equilibrium of the electric charge condition is reestablished by electron transfer, for example, by discharge.

It means generation of an extremely high-density energy field, and when the collapsing is performed in water, it is accompanied with generation of free radical species ~~by~~ as a result of the decomposition of ambient water molecules. In addition, because the electric charge carriers are OH^- and H^+ ,

~~the generated free radical species—such as~~ are $\cdot \text{OH}$ and $\cdot \text{H}$ ~~are formed by through the neutralization of electric charges by discharge charge.~~

~~The~~Since the free radical ~~species, which~~ species are very highly reactive, they react with various compounds dissolved or suspended in solution, and it results in changing composition or decomposing the compounds in solution. Because an extreme reaction field ~~at~~ of ultrahigh temperature and ultrahigh pressure is formed during collapsing, it becomes possible to sterilize microorganisms such as microbes and viruses and to decompose aromatic compounds such as phenol, although it was hitherto regarded as impossible. Examples of the substances decomposed by collapsing include almost all organic compounds, inorganic compounds such as FeSO_4 , CuNO_3 , AgNO_3 , and MnO_2 ; dioxins PCBs, chlorofluorocarbons microbes, viruses, and the like.

Hereinafter, the method for collapsing the micro bubbles will be described.

Figure 5 is a side view illustrating an apparatus for collapsing the microbubbles by discharge. The microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas is injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. An anode 21 and a cathode 22 are placed in the container 1, and the anode 21 and the cathode 22 are connected to a discharger 2.

First, microbubbles are generated in the container 1

containing a solution by using the microbubble generator 3. The solution in the container 1 used for generation of microbubbles is preferably water (distilled water, tap water, or the like), seawater, or the like; ~~but~~ and an organic solvent such as oil, alcohol, acetone, toluene, or petroleum oil may also be used. In the present specification, water is used as the solution for convenience in description, but the present invention is not limited thereto.

The electric discharge is generated in the solution ~~is discharged in~~ of the container 1 by using the discharger 2. A ~~saturation bubble~~ For more effective collapsing, the microbubble concentration of microbubbles in the container 1 is preferably 50% or more of the saturated condition of microbubbles, ~~for more effective collapsing during the underwater discharge.~~ In addition, the voltage of the underwater discharge is preferably 2,000 to 3,000 V. The stimulation ~~of~~ caused by the underwater discharge ~~raises~~ accelerates the decreasing speed of ~~microbubble~~ the size decrease by natural dissolution of the microbubbles ~~in water~~ and results in collapsing (disappearance) the bubbles. Extreme reaction fields are formed and free radicals such as $\cdot\text{OH}$ and $\cdot\text{H}$ are formed by decomposition of water, simultaneously with disappearance of microbubbles, and the substances and others present in water are decomposed.

The gas used for generation of micro bubbles in the microbubble generator 3 is not particularly limited, and ~~may be,~~ ~~or alternatively,~~ the microbubbles may be generated with ozone or oxygen. Microbubbles generated with oxygen or ozone show higher in oxidative potential and result ~~results~~ in generation of a greater number of free radical species during ~~collapsing,~~ and collapsing. These gases give an action to decompose a superior achievement in the decomposition of hazardous

substances and others superior both in the quantitative and qualitative points as well as as a sterilizing action in sterilization. Alternatively, the microbubbles may be generated after oxygen or ozone is previously contained in the solution in the container.

Hereinafter, a method for collapsing the microbubbles by ultrasonication will be described. Description on the devices the same as those described in the method for collapsing the microbubbles by discharge will be omitted.

Figure 6 is a side view illustrating an apparatus for collapsing the microbubbles by ultrasonic wave. A microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. An ultrasonicator 4 is installed on the container 1. The installation site of the ultrasonicator 4 is not particularly limited, but preferably between the intake 31 and the microbubble-containing solution outlet 32, for more efficient collapsing the microbubbles.

Microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

Then, an ultrasonic wave is irradiated on the microbubble-containing water in the container 1 by using the ultrasonicator 4. During For more effective collapsing by the ultrasonic wave irradiation, ~~the microbubbles by ultrasonic wave irradiation,~~ the saturation bubble microbubble concentration of microbubbles

in the container 1 is preferably 50% or more, ~~for more effective collapsing the~~ of the saturated condition of microbubbles. Ultrasonic wave irradiation at a saturation bubble concentration of 50% or more leads to more efficient collapsing. The irradiation frequency of the ultrasonic wave is preferably 20 kHz to 1MHz; and the exposure time of ultrasonic wave is preferably 30 seconds or less, but the irradiation may be continued for an extended period of time.

~~In the~~As a conventional methods of destructing hazardous substances and others by ultrasonic wave, which were simple irradiation of ultrasonic wave on normal water, lower in the efficiency of method, an ultrasonic wave has been used to decompose toxic substances. In this case, the ultrasonic wave is simply irradiated into normal water and the amount of generating free radicals ~~by collapsing, and thus had an insufficient action, it was not possible~~ is not enough to decompose aromatic compounds such as ~~phenol; but~~ phenol. But, it became possible to ~~destruct~~ disinfect microbes, viruses, and to decompose aromatic compounds such as phenol, which were not possible hitherto, by collapsing the microbubbles by irradiating ultrasonic wave on the microbubbles as in the present invention.

Hereinafter, a method for collapsing the micro bubbles by swirling current will be described. Description on the devices the same as those in the method for collapsing the microbubbles by electrical discharge ~~pressure~~ and the method for collapsing the microbubbles by ultrasonication will be omitted.

Figure 7 is a side view illustrating an apparatus for collapsing the microbubbles by swirling current. A microbubble generator 3 takes in the solution in a container 1 though an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for

injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. A circulation pump 5 is connected to the container 1 for partial circulation of the microbubble-containing solution in the container 1, and an orifice having multiple holes (porous plate) 6 is placed in the pipe (circulation pipe) which is connected to the circulation pump 5 at one end and to the container 1 at the other end. Part of the microbubble-containing solution poured out of the circulation pipe is re-circulated by the circulation pump and an swirling current is formed during passage through the orifice (porous plate) 6.

First, microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

~~The~~A part of the microbubble-containing water is then fed into the circulation pump 5 for partial circulation. The microbubble-containing water is further fed by the circulation pump 5 to the orifice (porous plate) 6, and an swirling current is formed in the pipe downstream thereof. The microbubbles are crushed by expansion or compression of the microbubbles during passage and by the electric swirling current generated by the swirl of electrically charged microbubbles due to the swirling current generated in the pipe. The positions of the circulation pump 5 and the orifice (porous plate) 6 on the channel may be altered.

Although only one orifice (porous plate) 6 is shown in Figure 7, multiple orifices may be installed, and the circulation pump 5 may be eliminated as needed. Alternatively, the orifice 6 may be replaced with a punching plate. When a

circulation pump 5 is installed, the pressure (positive pressure) of compressing the solution toward the orifice (porous plate) 6 is preferably 0.1 MPa or more. A positive pressure of less than 0.1 MPa may lead to insufficient eddy current generation. In addition, the pump 5 gives a negative pressure lower than the environmental pressure in the upstream pipe.

Figure 8 is a side view illustrating a method for collapsing by using positive or negative pressure; and Figure 9 is a partially magnified drawing of the area of a punching plate 10 and a pump 9 (the arrow in Figure 9 indicates the direction of the flow of microbubble-containing solution). Description on the devices the same as those described above will be omitted.

As shown in Figure 8, it is an apparatus for collapsing of microbubbles by draining the microbubble-containing water discharged from a microbubble generator 3 through a punching plate 10. The punching plate 10 is placed between two microbubble-containing solution outlets 32 (between the container 1 and the microbubble generator 3). An intake 11 for compressing the microbubble-containing solution to a pump 9 is formed between the punching plate 10 and the container 1 in the microbubble-containing solution outlet 32. Part of the microbubble-containing solution taken in into the intake 11 is fed to the pump 9 and then further forward by the pressure of the pump 9. The microbubble-containing solution is fed by the pump 9 via an outlet port 12 formed between the microbubble generator 3 and the punching plate 10 into the microbubble-containing solution outlet 32, and passes through the punching plate 10 once again. Thus, it is possible to crush the microbubbles by performing internal circulation forcibly by the pump 9 and increasing the swirling current drastically during passage through the punching plate 10. The positive pressure of

the pump 9 is preferably adjusted to 0.1 MPa or more for ~~forcibly~~ the forcible internal circulation of the microbubble-containing solution in the microbubble-containing solution outlet 32. A positive pressure of pump 9 of less than 0.1 MPa ~~results in inefficient~~ may lead to the generation of insufficient internal circulation. The pump 9 also give a negative pressure lower than the environmental pressure in the intake side (intake 11). The positive pressure is a pressure higher than the environmental pressure, i.e., a pressure of the pump 9 feeding the solution, while the negative pressure is a pressure lower than the environmental pressure, i.e., a pressure generated when the pump 9 takes in the solution.

Multiple punching plates 10 may be installed according to application, and multiple pumps 9 may be installed as needed in the method for collapsing the microbubbles shown in Figures 8 and 9. In addition, for example, a check valve may be installed in the microbubble-containing solution outlet 32 as needed.

Hereinafter, a method for collapsing the microbubbles by using the catalytic action of an oxidizer during its reaction. Description on the devices the same as those described above will be omitted.

Figure 10 is a side view illustrating an apparatus for collapsing the microbubbles by using the catalytic action of an oxidizer during its reaction. A microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this

way, microbubbles are generated in the container 1. An oxidizer-supplying unit 7 is connected to the container 1, and an oxidizer is supplied therefrom into the container 1.

Microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

Then, a catalyst is added to the container 1. Favorable examples of the catalysts include various catalysts known in the art, including metal catalysts such as copper, palladium, iron, vanadium, tin, titanium, zirconium, platinum, manganese, cobalt, nickel, rubidium, rhodium, and zinc; these catalysts may be used alone or in combination of two or more; and copper is more preferable. The microbubbles may be generated after addition of the catalyst into the container 1.

An oxidizer is supplied from the oxidizer-supplying unit 7. The oxidizer is not particularly limited, and anyone of various known oxidizers such as ozone, hydrogen peroxide, sodium hypochlorite, manganese dioxide, sulfuric acid, nitric acid, potassium permanganate, copper chloride, and silver oxide may be used favorably; these oxidizers may be used alone or in combination of two or more; and in particular, ozone and hydrogen peroxide are more preferable.

Supply of an oxidizer into the container 1 results in generation of very high oxidative radicals in the reaction between the oxidizer and the catalyst. The radicals accelerate collapsing the microbubbles by their collision to the microbubbles. Although it is possible to decompose hazardous substances contained in water in the reaction between the oxidizer and the catalyst, it became possible to decompose hazardous substances more efficiently and also to decompose and sterilize microorganisms such as microbes and viruses, by the collapsing the microbubbles by using the catalytic action

associated with the reaction between the oxidizer and the catalyst.

Hereinafter, the methods for collapsing the microbubbles will be described with reference to Examples, but it should be understood that the present invention is not restricted thereby.

EXAMPLES

Example 1

10 L of phenol-containing water was placed in the container 1 shown in Figure 5. Microbubbles~~are~~ were generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. The microbubbles were formed continuously, while the~~saturation bubble~~ concentration of microbubbles in the container~~is controlled to 1~~ was controlled to 50% or more of the saturation.

Then, the water was electrically discharged at a voltage of 2,400 V ten times per 10 minutes by the discharger 2, for collapsing the microbubbles.

~~Analysis of the water during collapsing by ESR gave the spectrum shown in Figure 11, confirming~~Figure 11 shows the ESR spectrum of the water during collapsing and conforms the presence of free radical species therein. The ESR spectrum shown in Figure 11 is determined, as a spin-trapping agent 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) is added to the sample. The results demonstrated generation of free radicals.

After the collapsing the microbubbles, phenol~~had been~~ was decomposed completely.

Example 2

10 L of phenol-containing water was placed in the container

1 shown in Figure 6. Microbubbles~~—are~~ were generated in the microbubble generator 3 by using ozone as the gas for preparation of micro bubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the~~—saturation—bubble~~ concentration of microbubbles in the container~~—was controlled to~~ 1 was controlled to 50% or more of the saturation.

Then, the microbubbles are crushed by irradiation of an ultrasonic wave at an irradiation frequency of 200 kHz by the ultrasonicator 4 for 10 minutes. ESR spectral analysis of the water during collapsing~~—similar to that in Example 1 gave an ESR spectrum~~ indicates that the result is similar to that shown in Figure 11.

Phenol~~—had been~~ was decomposed completely after the collapsing the microbubbles.

Example 3

10 L of phenol-containing water was placed in the container 1 shown in Figure 7. Microbubbles~~—are~~ were generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the~~—saturation—bubble~~ concentration of microbubbles in the container~~—was controlled to~~ 1 was controlled to 50% or more of the saturation.

Then, the microbubble-containing water in the container 1 was circulated partially, and part of the microbubble-containing water was introduced into the circulation pipe connected to the circulation pump 5. The microbubble-containing water introduced into the circulation pump 5 was fed to the orifice (porous plate) 6 at a positive pressure of 0.3 MPa, allowing the

microbubbles crushed by the swirling current generated there.

ESR spectral analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol—~~had been~~ was decomposed completely after the collapsing the microbubbles.

Example 4

10 L of phenol-containing water was placed in the container 1 shown in Figure 8. Microbubbles—~~are~~ were generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the—~~saturation bubble~~ concentration of microbubbles in the container—~~was controlled to~~ 1 was controlled to 50% or more of the saturation.

Then, part of the microbubble-containing water discharged from the microbubble generator 3 and passing out of the punching plate 10 was taken in through the intake 11 and fed to the discharge side by operation of the pump 9—~~and fed by the pump 9 to the discharge side,~~ for forcibly internal circulation thereof in the microbubble-containing solution outlet 32. The positive pressure of the pump 9 then was 0.5 MPa. The microbubble-containing water fed by the pump 9 was made to pass through the punching plate 10 once again via the outlet port 12. Such an internal circulation raised the swirling-current efficiency drastically and was effective in collapsing the microbubbles.

ESR spectrum analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol—~~had been~~ was decomposed completely after the

collapsing the microbubbles.

Example 5

10 L of phenol-containing water was placed in the container 1 shown in Figure 10. Microbubbles~~are~~ were generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the~~saturation bubble~~ concentration of microbubbles in the container~~was controlled to~~ 1 was controlled to 50% or more of the saturation.

Then, 5 g of a powdery copper catalyst was placed in the container 1, and an ozone gas was supplied from the oxidizer-supplying unit 7 into the container 1. The amount of the ozone gas supplied was 1 g. The micro bubbles were crushed by the catalytic reaction associated with the reaction between the ozone gas and the copper catalyst when the ozone gas was supplied.

ESR spectrum analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol~~had been~~ was decomposed completely after the collapsing the microbubbles.

Advantageous effects of the invention

Collapsing the micro bubbles by the method according to the present invention lead to increase in the speed of microbubbles size decrease due to utilization of a stimulation (discharge, ultrasonic wave, swirling current, positive and negative pressure, or the catalytic reaction associated with the

reaction of oxidizer, or the like), disappearance of microbubbles and generation of active oxygen species and free radical species for decomposition of substances present inside the microbubbles or in the area surrounding the microbubbles, and compositional change thereby of the chemical substances dissolved or floated in water; and thus, it became possible to sterilize microorganisms such as microbes, viruses, and others present in solution and decompose aromatic compounds such as phenol, which was difficult in the past, and thus, to decompose almost all hazardous substances and others.

Industrial applicability

By the collapsing the microbubbles according to the present invention, it became possible to sterilize microorganisms such as microbes, viruses, and others present in solution and decompose aromatic compounds such as phenol, which were difficult to decompose in the past, and the method is applicable in the fields for processing hazardous substances and the like.

ABSTRACT

A method for collapsing a microbubble ~~characterized in that it comprises~~ includes applying stimulation to the microbubble ~~in the step of~~ during the gradual decrease of the ~~its size, in a course wherein the~~ size. As a result, the microbubble floating in a solution that decreases in ~~its~~ size due to the natural dissolution of a gas contained in the microbubble and disappears after a while, ~~to thereby enhance~~ has the speed of ~~the~~ its size decrease enhanced and ~~cause~~ causes the microbubble to disappear.